

**Color-developing Agent Resin Composition, Emulsion thereof and
Method for Preparing the Same**

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FIELD OF THE INVENTION

The present invention relates to a color-developing agent resin composition.

BACKGROUND OF THE INVENTION

10 Special color-developing resin agents for no-carbon copying paper and
methods for preparing such agent were studied in two process routes. The first route
gave emphasis on using the single structure of zinc salicylates. Though this kind of
resin has advantages of fast developing at a low temperature and developing good
bright colors, the defects are that color-developing strength is light and light-aging
15 resistance is poor, and the like. Representative examples include Japanese Laid-open
Application No. 11-129614 discloses ingredients of a color-developing agent and
pressure-sensitive copying materials prepared by using the color-developing agent.
Japanese Laid-open Application No. 10-217607 discloses ingredients of a
color-developing agent and pressure-sensitive copying materials prepared by using the
20 color-developing agent. Japanese Laid-open Application No. 2001-261628 discloses a
preparation method of multivalent metal salts of salicylic acid derivatives. Japanese
Laid-open Application No. 2001-261629 discloses a method for preparing salicylic
acid derivatives. Japanese Laid-open Application No. 2001-169424 discloses a
method for preparing salicylic acid derivatives. Japanese Laid-open Application No.
25 2000-109448 discloses a method for preparing salicylic acid derivatives. Japanese
Laid-open Application No. 2000-239224 discloses a method for preparing salicylic
acid derivatives. Japanese Laid-open Application No. 2000-168231 discloses a
method for preparing a color-developing emulsion used for pressure-sensitive paper.
Japanese Laid-open Application No. 6-135132 discloses a method for preparing a
30 color-developing emulsion used for pressure sensitive paper. Japanese Laid-open
Application No. 6-293699 discloses a method for preparing salicylic acid derivatives
and the use of metal salts thereof in color-developing agent. Japanese Laid-open
Application No. 8-53536 discloses a method for preparing multivalent metal salts of

salicylic acid resin and the use thereof. Japanese Laid-open Application No. 6-227117 discloses a method for preparing salicylic acid derivatives and the use of metal salts thereof in color-developing agent and the like.

Additionally, Chinese Patent Application Nos. 1031235A, 87107802A,
5 88102163A, 1229032A, 1247130A, 1276299A and 1040377A provide a single structure of zinc salicylate resins.

Another route emphasizes the single structure of phenolic resins. Though advantages of this kind of resin are that color-developing strength is heavy and light-aging resistance of writing is good, prominent disadvantages are that colors are
10 not bright, its coating yellows easily when it is exposed to the air, and developing speed at a low temperature is slow. Representative patents include U.S. Patent Nos. 54020185 and 5,017,546. The product is obtained by using an alkyl substituted phenol, formaldehyde and a metal compound as feedstocks to carry out the condensation reaction.

Chinese Patent Application No. 1200378A discloses a novel color-developing agent resin composition that is a blend of graft copolymers of a multivalent metal salt of an organic carboxylic acid and a phenolic resin. That application overcomes defects of the two kind of color-developing resin agents aforesaid. However, the composition still has disadvantages that developing speed at a low temperature is slow, colors are
15 not bright, and the emulsion is difficult to stabilize.
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SUMMARY OF THE INVENTION

The present invention illustrates a novel color-developing agent resin composition. The main component of the composition is a blend of graft copolymers
25 of a multivalent metal salt polymer of an aryl carboxylic acid and a phenolic resin. The composition is used as a color-developing agent for no-carbon copying paper in order to overcome defects of both kinds of the resin color-developing agents aforesaid.

The present invention also illustrates a novel color-developing agent resin
30 emulsion. It has the novel color-developing agent resin composition of the present invention as a main component.

Embodiments of the present invention include methods for preparing the novel color-developing agent resin composition of the present invention.

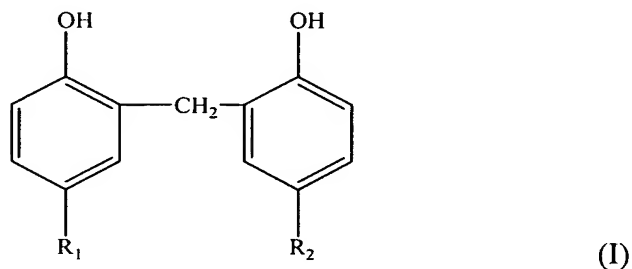
Other embodiments of the present invention include methods for preparing the novel color-developing agent resin emulsion of the present invention.

The present invention illustrates that the defects of previous color-developing agent resin compositions may be overcome by introducing a special structure of long chain alkenyl benzene. The present invention provides for a resin color-developing agent being formed, which has fast developing at a low temperature, bright color, heavy developing strength, good light-aging resistance of writing, and its coating is difficult to turn yellow.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

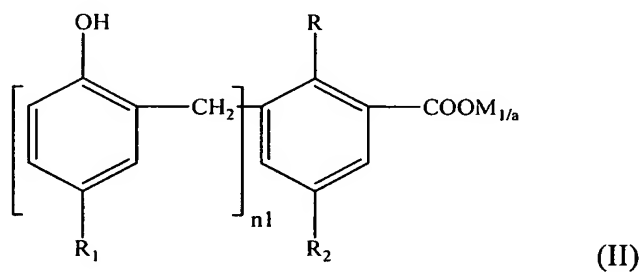
The present invention relates to a color-developing agent resin composition which contains:

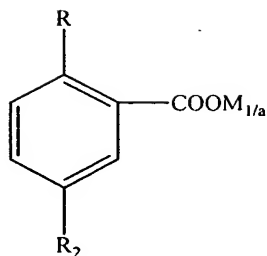
(1) A phenolic resin represented by formula (I) as follows:



and

(2) A blend of graft copolymers of a phenolic resin and a multivalent metal salt polymer of a substituted aryl carboxylic acid, said graft copolymers are represented by formula II and III respectively as follows:





(III)

wherein,

R is C₁-C₄ linear alkyl, hydroxy or halogen;

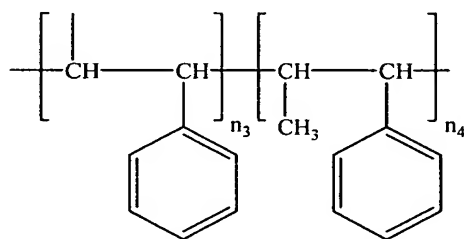
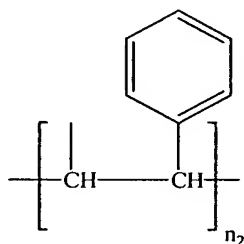
5 R₁ is each individually C₁-C₁₂ linear or branched alkyl, C₁-C₁₂ halohydrocarbyl, C₆-C₁₂ aryl, C₇-C₁₂ aralkyl;

n₁ = 1-2

M is a multivalent metal ion;

a represents the valence of M;

10 R₂ has a structure as follows:



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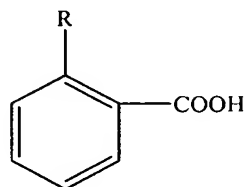
wherein n₂ is an integer of 1-100, preferably 1-10; n₃ + n₄ is an integer of 1-100, preferably 1-10.

The novel color-developing agent resin composition of the present invention is prepared through steps as follows:

20 (1) synthesizing the polymer of a substituted aryl carboxylic acid and an alkenyl benzene in the presence of a catalyst in an inert solvent by using the

substituted aryl carboxylic acid or ester having a general formula (IV) as follows and an alkenyl benzene as feedstocks, and reacting the polymer with a multivalent metal ion to form a multivalent metal salt polymer of substituted aryl carboxylic acid as an intermediate;

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(IV)

wherein, the definition of R is the same as that above;

(2) melting the mixture of a *p*-substituted phenol, the substituted aryl carboxylic acid having a general formula (IV), a metal oxide and a catalyst, and reacting them;

(3) adding the intermediate of step 1 to the reaction product of step 2, and reacting at 80-150 °C for 30-150 minutes;

(4) reacting the reaction product of step 3 with an aldehyde under refluxing at 80-130 °C for 1-10 hours;

(5) dehydrating the reaction product of step 4 at a temperature of 90-150 °C under vacuum at 0.02-0.06 mPa; and

(6) cooling the dehydrated product and milling to reach a required particle size range.

Wherein, the molar ratio of the substituted aryl carboxylic acid to *p*-substituted phenol is 0.05-1.55:1; the molar ratio of the metal oxide to substituted aryl carboxylic acid in step 2 is 0.02-1.30:1; the molar ratio of the metal salt of substituted aryl carboxylic acid to *p*-substituted phenol in step 3 is 0.05-5.0:1; the molar ratio of the aldehyde to *p*-substituted phenol in step 4 is 0.06-2.0:1. It is desirable that the reaction is carried out under the protection of N₂ atmosphere.

The *p*-substituted phenol used for the preparation includes a linear chain alkyl- or isomeric alkylphenol, arylphenol, aralkylphenol or the mixture thereof, halogenated phenol and the like. In particularly, it includes *p*-methylphenol, *p*-ethylphenol, *p*-propylphenol, *p*-butylphenol, *p*-tert-butylphenol, *p*-amylphenol, *p*-hexylphenol, *p*-heptylphenol, *p*-octylphenol, *p*-tert-octylphenol, *p*-nonylphenol, *p*-decylphenol,

p-undecylphenol, *p*-dodecylphenol, and their isomers, *p*-chlorophenol, *p*-bromophenol, *p*-phenylphenol, *p*-phenyl alkylphenol and the like.

Said alkenyl benzene includes vinyl benzene, propenyl benzene, isopropenyl benzene, butenyl benzene, isobutenyl benzene, butadienyl benzene and the like.

5 Said substituted aryl carboxylic acid includes: C₁-C₄ linear alkylphenyl carboxylic acid, halophenyl carboxylic acid, salicylic acid and esters thereof.

Said metal oxide includes oxides of the following metals: Ca, Mg, Ba, Cu, Cd, Al, Zn, Cr, In, Sn, Co, Ni, Ti and the like.

10 Said aldehyde includes: formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, amylaldehyde, benzaldehyde and the like. The most often used is a formalin of 37% or 50% by weight.

Said inert organic solvent is one that contains no benzene such as organochlorines, alcohols, ethers, ketones and the like. In particularly, it includes chloroethane, dichloroethane, trichloromethane, methanol, ethanol, propanol, butanol,
15 isopropanol, isobutanol, dipropyl ether, diisopropyl ether, dibutyl ether, diisoamyl ether, acetone, butanone, pentanone, hexanone, hexanedione, heptanone, cyclohexanone and the like.

Said the multivalent metal salt polymer of substituted aryl carboxylic acid is preferably the polymer of zinc salt.

20 Said catalyst is generally acidic or basic catalyst, or a given surfactant.

In the presence of an emulsifying agent, the color-developing agent resin composition of the present invention is emulsified in an emulsifying machine to obtain an oil-in-water emulsion with the average particle size less than 1.5 μm.

25 The CF coating formulated by using the resin emulsion of the present invention is compared with CF coatings formulated by using resins of HRJ 14508 (as comparative product 1) sold by an American corporation in the international market and 80H (as comparative product 2) sold by a Taiwan corporation respectively. The results are obtained as follows:

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Table 1 Comparison of CF coatings formulated by using
different resin color-developing agents for developing strength.
(Humidity RH 43% at a temperature of 20 °C)

Resin	Developing value			Amount coated g/m ²
	ΔE 10 sec.	ΔE 1 min	ΔE 24 hr	
Comparative product 1	68.16	74.62	76.68	5.58
Comparative product 2	76.76	77.29	80.79	5.76
The present invention	81.58	81.86	84.91	5.60

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Table 2 Comparison of CF coatings formulated by using
different resin color-developing agents for developing speed
Humidity RH43% at a temperature of 20 °C

Resin	Developing value		Differences	Amount coated g/m ²
	ΔE 10 sec.	ΔE 1 min	ΔE 1 min-10 sec	
Comparative product 1	68.16	74.62	6.46	5.58
Comparative product 2	76.76	77.29	0.53	5.76
The present invention	81.58	81.86	0.28	5.60

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Table 3 Comparison of CF coatings formulated by using
different resin color-developing agents for light aging property
Humidity RH43% at a temperature of 20 °C

Resin	Light-aging of writing (UV lamp, for 4 hr)			Amount coated g/m ²
	Developing value before aging	Developing value after aging	Retention %	
Comparative product 1	76.68	66.41	86.60	5.62
Comparative product 2	80.79	71.74	88.80	5.57
The present invention	84.91	74.40	87.20	5.54

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Table 4 Comparison of light-aged CF coatings formulated by using
different resin color-developing agents for developing value
Humidity RH43% at a temperature of 20 °C

Resin	Light-aging of coatings (UV lamp, printed after 4 hr)			Amount coated g/m ²
	ΔE 10 sec.	ΔE 1 min	ΔE 24 hr	
Comparative product 1	56.91	68.65	74.30	5.80
Comparative product 2	72.99	74.15	76.74	5.75
The present invention	78.50	79.23	80.09	5.77

Test conditions:

1. An EPSEN-III type printer was used for all printing with 3rd gear and 4th couplet.

2. Developing value was measured by using SC-80 Model of color difference meter produced by Beijing Kang guang Corporation.

3. CF formulation was used with the same formulation and coated by hand.

4. CF formulation:

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Water	70 ml
Dispersant agent	1.3 g
Porcelain clay	17.5 g
Calcium carbonate	18 g
Calcined porcelain clay	8.5 g
Starch gel(12%)	65 ml
Resin	17 g
SBR latex	8 g

5. Testing procedure for data: CF slurry was formulated according to CF formulation and coated onto a sheet of paper by hand, then the coated paper was dried in air and weighted, and the amount coated was calculated. After printing was
 10 completed on the EPSSEN-III type printer with 3rd gear and 4th couplet, developing value was measured by using SC-80 Model of color difference meter and the humidity, temperature and aging condition were recorded.

The present invention is further illustrated through examples as follows:

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Example 1:

By adding 300 parts by weight of salicylic acid, 300 parts by weight of isopropanol and 15 parts by weights of *p*-toluene sulfonic acid to an autoclave; adding 565 parts by weight of vinyl benzene within 5 hours through a high level tank at 80 °C; after feeding keeping the temperature and continuing the reaction under stirring
 20 for 2 hours; removing isopropanol, and adding 88 parts by weight of zinc oxide and reacting at 90 °C for 2 hours, the intermediate 1 was prepared to be used.

Example 2:

By adding 300 parts by weight of salicylic acid, 400 parts by weight of
 25 dichloroethane and 30 parts by weight of sulfuric acid to an autoclave; adding 512 parts by weight of propenyl benzene within 7 hours under stirring at 50 °C through a high level tank; after feeding keeping the temperature and continuing the reaction under stirring for 2 hours; adding 490 parts by weight of 5% sodium hydroxide to

neutralize sulfuric acid; removing the water layer; washing the resultant material with 500 parts by weight of water; removing the water layer; distilling off dichloroethane; and then adding 90 parts by weight of zinc oxide and reacting at 95 °C for 4 hours, the intermediate 2 was prepared to be used.

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Example 3:

By adding 300 parts by weights of salicylic acid, 500 parts by weight of cyclohexanone, 10 parts by weight of zinc chloride to an autoclave; adding 580 parts by weight parts by weight of butadienyl benzene within 4 hours through a high level
10 tank under stirring at 70 °C; after feeding keeping the temperature and continuing the reaction under stirring for 2 hours; removing cyclohexanone; adding 95 parts by weight of zinc oxide and reacting at 100 °C for 6 hours, the intermediate 3 was prepared to be used.

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Example 4:

By adding 300 parts by weight of methyl salicylate, 600 parts by weight of trichloromethane and 40 parts by weight of sulfuric acid to an autoclave; adding 334 parts by weight of butenyl benzene within 5 hours at 50 °C through a high level tank; after feeding keeping the temperature and continuing stirring for 2 hours; then adding
20 283 parts by weight of a 45% aqueous sodium hydroxide solution to hydrolyze for 4 hours while controlling the temperature at 100 °C; neutralizing the reaction mixture with sulfuric acid solution to pH 6; separating the water layer; washing the oil layer with 500 parts by weight of water, and distilling off trichloromethane; adding 80 parts by weight of zinc oxide and reacting at 100 °C for 6 hours, the intermediate 4 was
25 prepared to be used.

Example 5:

By adding 180 parts by weight of tert-butylphenol, 25 parts by weight of salicylic acid and 8 parts by weight of zinc oxide to an autoclave; heating to melt the
30 resultant mixture until all the materials were molten; adding 520 parts by weight of the intermediate 1; reacting for 1.5 hours while controlling the reaction temperature at 95 °C; adding 50 parts by weight of formaldehyde, then keeping the autoclave temperature at 102 °C to reflux for 1 hour; dehydrating under a vacuum at 0.07 mPa

for 5 hours, and then discharging, cooling and milling, the color-developing agent resin composition 1 was obtained .

Example 6:

5 By adding 247 parts by weight of sec.-octylphenol, 40 parts by weight of salicylic acid, 12 parts by weight of zinc oxide and 8 parts by weight of *p*-toluene sulfonic acid to an autoclave; heating to melt the resultant mixture until all the materials were molten; adding 416 parts by weight of the intermediate 2; reacting for 1 hour while controlling the reaction temperature at 100 °C; adding 100 parts by
10 weight of formaldehyde, then keeping the autoclave temperature at 102 °C to reflux for 2 hours; dehydrating under a vacuum at 0.06 mPa for 7 hours, and the discharging, cooling and milling, the color-developing agent resin composition 2 was obtained.

Example 7

15 By adding 308 parts by weight of *p*-chlorophenol, 50 parts by weight of salicylic acid, 15 parts by weight of zinc oxide and 5 parts by weight of *p*-toluene sulfonic acid to an autoclave; heating to melt the resultant mixture until all the materials were molten; adding 624 parts by weight of the intermediate 3; reacting for 1 hour while controlling the reaction temperature at 105 °C; adding 100 parts by
20 weight of formaldehyde, then keeping the autoclave temperature at 100 °C to reflux for 3 hours; dehydrating under a vacuum at 0.04 mPa for 8 hours, and then discharging, cooling and milling, the color-developing agent resin composition 3 was obtained.

Example 8:

25 By adding 342 parts by weight of *p*-phenylphenol, 50 parts by weight of salicylic acid, 14 parts by weight of zinc oxide and 3 parts by weight of *p*-toluene sulfonic acid to an autoclave; heating to melt the resultant mixture until all the materials were molten; adding 408 parts by weight of the intermediate 4; reacting for
30 30 minutes while controlling the reaction temperature at 110 °C; adding 120 parts by weight of formaldehyde, then keeping the autoclave temperature at 100 °C to reflux for 3 hours; dehydrating under a vacuum at 0.04 mPa for 8 hours, and then

discharging, cooling and milling, the color-developing agent resin composition 4 was obtained.

Example 9:

5 By heating 400 parts by weight of the resin composition 1 prepared in Example 5 above, 28 parts by weight of polyvinyl alcohol, 2 parts by weight of a surfactant and 500 parts by weight of water at 120 °C for 2 hours; emulsifying and dispersing for 40 minutes to make the materials change from the water-in-oil type into the oil-in-water type; cooling the resultant emulsion to 40 °C and then discharging,
10 checking and packaging, the color-developing agent resin emulsion 1 was obtained. Its performances are shown in Table 5:

Example 10:

Taking the same steps as those in Example 9, except that the color-developing
15 agent resin compositions 2-4 were used instead of the color-developing agent resin composition 1, the color-developing agent resin emulsions 2-4 were obtained respectively. Their performances are shown in Table 5:

Example 11:

20 By heating 393 parts by weight of the resin composition 1 obtained in Example 5 above, 36 parts by weight of a modified starch, 1 parts by weight of a surfactant and 500 parts by weight of water at 120 °C for 2 hours; emulsifying and dispersing them for 40 minutes to make the materials change from W/O into O/W type; then cooling the emulsion to 40 °C, and discharging, checking and packaging,
25 the color-developing agent resin emulsion 5 was obtained. Its performances are shown in Table 5:

Comparative Example 1

By adding 700 parts by weight of *p*-butylphenol, 130 parts by weight of
30 salicylic acid, 30 parts by weight of zinc oxide, 2.0 parts by weight of ethyl benzenesulfonic acid; heating to melt them until all the materials were molten; adding 90 parts by weight of formaldehyde; then keeping the autoclave temperature at 100 °C to reacting under refluxing for 4 hours; adding 80 parts by weight of a salt of an

organic carboxylic acid to react for 1 hour; dehydrating under a vacuum at 0.04 mPa while keeping the dehydration temperature at 120 °C until the dehydration was completed, then discharging, cooling, milling, emulsifying and dispersing, the comparative emulsion 1 was obtained. Its performances are shown in Table 5:

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Table 5 Comparison of the color-developing agent emulsions of Examples for color-developing performances

Humidity RH43% at a temperature of 20 °C

Sample	Developing speed, ΔE 1 min-10sec	Developing strength, ΔE 24 hr
Color-developing agent emulsion 1	0.52	87
Color-developing agent emulsion 2	0.59	88
Color-developing agent emulsion 3	0.45	87
Color-developing agent emulsion 4	0.35	86
Color-developing agent emulsion 5	0.30	87
Comparative emulsion 1	2.80	86